

# Varying $\text{Eu}^{2+}$ magnetic order in $\text{EuFe}_2\text{As}_2$ by chemical pressure

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Among iron 122 pnictide superconductors, the  $\text{EuFe}_2\text{As}_2$  series draws particular interest because, in addition to superconductivity or the long-range spin-density-wave order in the Fe subsystem, the localized  $\text{Eu}^{2+}$  magnetic moments order at low temperatures. Here we present a novel scheme of how the spins align in the Eu compounds when pressure varies the coupling; we explain magnetization measurements on  $\text{EuFe}_2(\text{As}_{1-x}\text{P}_x)_2$  single crystals as well as other observations of the  $\text{Eu}^{2+}$  ordering previously reported in literature. The magnetic moments of the  $\text{Eu}^{2+}$  ions are slightly canted even in the parent compound  $\text{EuFe}_2\text{As}_2$ , yielding a ferromagnetic contribution along the  $c$ -direction that becomes stronger with pressure. Reducing the interlayer distance even further, the antiferromagnetic coupling of the  $ab$  planes finally turns ferromagnetic.

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With the discovery of superconductivity in iron pnictides, a new approach was taken towards understanding the mechanism of high-temperature superconductivity. Magnetism seems to be the crucial factor determining the physical properties, as superconductivity emerges with the suppression of the spin-density-wave (SDW) ordering in the FeAs layers.<sup>1</sup> Although the highest critical temperatures  $T_c$  are reached in the quaternary 1111 compounds, the ternary 122 compounds quickly advanced as the model systems of iron pnictides due to the availability of good single crystals. Besides the parent compounds  $\text{BaFe}_2\text{As}_2$  and  $\text{SrFe}_2\text{As}_2$ ,  $\text{EuFe}_2\text{As}_2$  is an outstanding member of the 122 series with a maximum  $T_c = 32$  K in  $\text{Eu}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$ ,<sup>2</sup> because in addition to the antiferromagnetic (AFM) order of the itinerant electrons in the FeAs layers at  $T_{\text{SDW}} = 189$  K, magnetic order of the localized  $\text{Eu}^{2+}$  ions is observed at low temperatures.  $\text{Eu}^{2+}$  possesses a large magnetic moment ( $J = 7/2$ ) that leads to a so called “A-type” AFM ordering below  $T_N = 19$  K,<sup>3-5</sup> meaning that the  $\text{Eu}^{2+}$  moments align ferromagnetically along the  $a$ -axis and antiferromagnetically along the  $c$ -axis. The coexistence and interplay of the second magnetic ordering with the SDW in the FeAs layers is drawing increasing attention.

Charge-carrier doping on the Eu- or Fe-sites,<sup>2,6,7</sup> isovalent P substitution on the As site<sup>8</sup> and physical pressure<sup>9,10</sup> change the  $\text{Eu}^{2+}$  ordering as well as the electronic properties of the system, eventually leading to superconductivity. One interesting signature of these superconductors is a resistivity re-entrance below  $T_c$  in the range of the  $\text{Eu}^{2+}$  ordering temperature, observed for example in  $\text{Eu}(\text{Fe}_{0.89}\text{Co}_{0.11})_2\text{As}_2$ ,<sup>7</sup>  $\text{EuFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$ ,<sup>8</sup> and  $\text{EuFe}_2\text{As}_2$  under pressure.<sup>9,10</sup> The re-entrance is suppressed by a magnetic field applied in the  $ab$ -plane, but not affected by a field parallel to the  $c$ -axis.<sup>7</sup> This implies that the  $\text{Eu}^{2+}$  ordering has noticeable impact on the superconductivity in the FeAs layers and that the Eu 122 compounds reveal an extraordinary possibility to study

the interplay between magnetism and superconductivity.

It is therefore quite surprising that, at present, no clear picture exists how the ordering of the Eu spins changes with doping or pressure. Furthermore, it is still under debate which kind of  $\text{Eu}^{2+}$  magnetic ordering coexists with superconductivity and different phase diagrams have been proposed even for the same compound.<sup>11,12</sup> In the following we concentrate on  $\text{EuFe}_2(\text{As}_{1-x}\text{P}_x)_2$  and discuss the influence of chemical pressure on the alignment of the  $\text{Eu}^{2+}$  magnetic moments. We suggest that the Eu spins are slightly canted along the  $c$ -axis, causing an appreciable ferromagnetic (FM) contribution that increases with pressure. Our scheme is consistent with published data and explains the apparent discrepancies in phase diagrams of Eu magnetic ordering.

## I. EXPERIMENTAL RESULTS

$\text{EuFe}_2(\text{As}_{1-x}\text{P}_x)_2$  single crystals used in this study were synthesized by a Bridgman method and characterized as previously described.<sup>11</sup> Optical investigations on crystals with  $x = 0$  and  $x = 0.18$  have been already reported.<sup>13,14</sup> Here we describe the magnetic behavior of  $\text{EuFe}_2\text{As}_2$  and  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$ , measured with a Quantum Design MPMS-XL superconducting quantum interference device (SQUID). We provide a complete characterization as a function of temperature ( $T$ ) and magnetic field ( $H$ ) for the main crystallographic directions.  $\text{EuFe}_2\text{As}_2$  has orthorhombic symmetry with  $a$  and  $b$  axes virtually identical. Even though twinning of the crystals did not allow us a characterization in the  $ab$ -plane, neutron scattering data indicate that the  $\text{Eu}^{2+}$  moments align along the  $a$ -direction. In Fig. 1 the temperature-dependent magnetization of  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$  is plotted for  $H = 20$  Oe, measured parallel and perpendicular to the  $ab$ -plane. While at elevated temperatures ( $T < T_{\text{SDW}}$ ) the paramagnetic

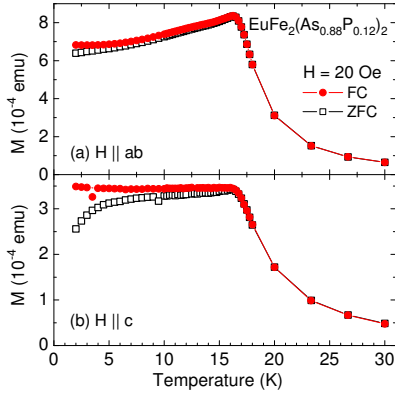


FIG. 1: Zero-field cooled (ZFC) and field-cooled (FC) magnetization curves (solid red circles and open black squares, respectively) for  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$ , measured in  $H = 20$  Oe parallel (a) and perpendicular (b) to the  $ab$ -plane.

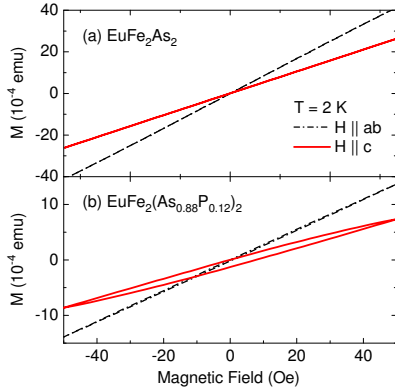


FIG. 2: Isothermal magnetization *versus* external magnetic field applied parallel (black dashed lines) and perpendicular (red solid line) to the  $ab$ -plane for  $T = 2$  K. (a) While for  $\text{EuFe}_2\text{As}_2$  no hysteresis can be observed, (b) in the case of  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$  the hysteresis is obvious for  $H \parallel c$  but can also be identified for  $H \parallel ab$ .

regime can be nicely described by the Curie-Weiss law, similar to the parent compound,<sup>13</sup> the cusp at  $T_N = 16$  K evidences AFM order of the  $\text{Eu}^{2+}$  moments. At low temperatures we find a distinct difference between the field-cooled (FC) and zero-field cooled (ZFC) behavior (especially for  $H \parallel c$ ) that seems to be more pronounced as P substitution increases.<sup>11</sup>

To clarify this point, we measured the field dependence of the magnetization parallel and perpendicular to the  $ab$ -plane. The complete magnetization *versus* field curve has already been discussed<sup>3,12</sup> and here we concentrate on the low-field features. Fig. 2 displays the results obtained at  $T = 2$  K for  $\text{EuFe}_2\text{As}_2$  and  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$ . While we observe no hysteresis for the parent compound,  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$  exhibits clear evidence of FM behavior when the magnetic field is applied parallel to the  $c$ -axis. For  $H \parallel ab$  only a much smaller hysteresis is observed. The hysteresis becomes narrower with increasing

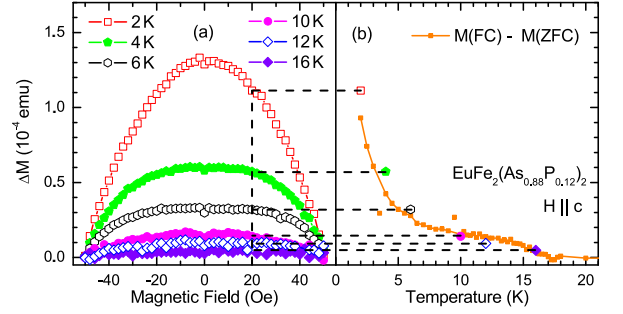


FIG. 3: (a) Height of the hysteresis for  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$ , measured with  $H \parallel c$  for different fields and temperatures. (b) Temperature dependence of the difference between the ZFC and FC curves shown in Fig 1(b). This difference can be compared to the hysteresis height at  $H = 20$  Oe shown in (a). The broken lines are a guide to the eye to stress the correlation between the two trends.

temperature and completely vanishes at 16 K (Fig. 3), which is the magnetic transition temperature common to both crystal directions. To follow the opening of the hysteresis, we plot in Fig. 3 the difference  $\Delta M$  between the magnetization curves acquired by sweeping the field down and up (*i.e.* the hysteresis height). The curves show a decrease of the hysteresis height on raising the temperature and it is instructive to compare this trend with the difference between the ZFC and FC curves at the same field. As shown in Fig. 3(b) the two trends coincide, demonstrating the development of magnetic ordering.

## II. MODEL

Based on these magnetization measurements and in agreement with other studies, we propose that the magnetic moments of the  $\text{Eu}^{2+}$  ions change their alignment under pressure as displayed in Fig. 4. In the parent compound, the spins orient along the  $a$ -direction, but basically reverse the direction in adjacent  $ab$ -planes.<sup>3</sup> More precisely, one observes canted AFM causing a small FM component of the moments in  $c$ -direction that is usually neglected in the discussion. Mössbauer studies reveal a steep increase of this canting angle with increasing P substitution until the Eu spins are aligned almost perpendicular to the  $ab$ -plane.<sup>12</sup> We want to emphasize that this has a huge impact on magnetic susceptibility and has to be considered in the interpretation.

Due to the non-negligible tilt angle out of the  $ab$ -plane, as displayed in Fig. 4, one always observes a FM signal along the  $c$ -axis, including a hysteretic behavior. This is exactly what we measured in our  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$  single crystal. The small hysteresis visible for  $H \parallel ab$  is likely caused by our limited precision in crystal alignment and we will not discuss it further. The fact that in the parent compound the hysteresis cannot be resolved might be due to the extremely small spin canting. Since chemical and physical pressures have a similar effect on

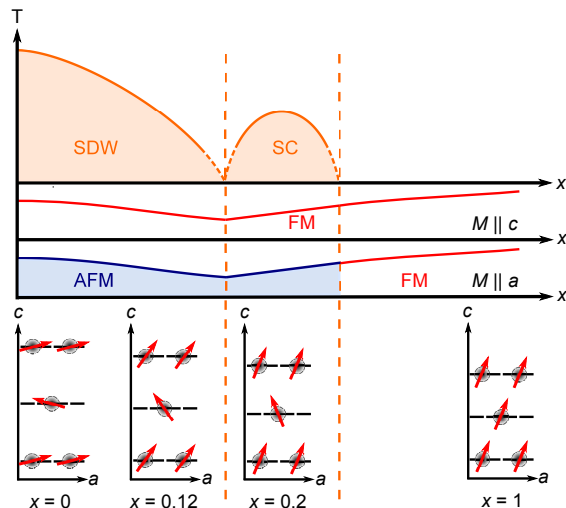


FIG. 4: Schematic phase diagram of  $\text{EuFe}_2(\text{As}_{1-x}\text{P}_x)_2$  indicating the SDW and SC phase. In the preceding panels, we distinguish between the Eu net magnetization along the  $a$ -axis ( $M \parallel a$ ) and along the  $c$ -axis ( $M \parallel c$ ) resulting from the present data and from Ref. 11,12. The scheme of the  $\text{Eu}^{2+}$  spin alignment is also shown. In the parent compound, A-type AFM is found with the spins being slightly canted towards the  $c$ -axis with an angle<sup>12</sup> of  $13^\circ$  to the  $ab$ -plane. Upon the application of pressure the canting angle increases until it saturates<sup>12</sup> at  $68^\circ$  with respect to the  $a$ -axis ( $x = 0.2$ ). At even higher pressure, the AFM interlayer coupling turns probably into a FM one.

the 122 compounds, we propose to examine  $\text{EuFe}_2\text{As}_2$  single crystals by a high-pressure SQUID susceptometer to confirm and complete the phase diagram. These measurements will reveal whether at higher pressure the AFM interlayer coupling finally turns into a FM one, as claimed for different Eu 122 compounds.<sup>6,11,12</sup> In Fig. 4 we also sketch the arrangement of the  $\text{Eu}^{2+}$  moments in the high-pressure limit ( $x = 1$ ).

### III. DISCUSSION

The hysteresis loop observed in our  $\text{EuFe}_2(\text{As}_{0.88}\text{P}_{0.12})_2$  single crystal measurements constitute the key to understand the various phase diagrams of Eu 122 pnictides proposed in literature. Since contributions from the  $c$ -direction are unavoidable in polycrystalline samples, a hysteresis is always seen as soon as the canting of the spins is pronounced enough. In the following we compare the phase diagram of Jeevan *et al.* based on single crystal measurements<sup>11</sup> with that of Nowik *et al.* who performed measurements on polycrystalline samples.<sup>12</sup> The former observe AFM  $\text{Eu}^{2+}$  ordering in the superconducting phase, whereas the latter group claims the coexistence of FM and superconductivity. The statements do not contradict each other since Jeevan *et al.* refer to the ordering of the  $\text{Eu}^{2+}$  moments in the  $ab$ -plane. If they measure along the  $c$ -axis, they will also

yield a phase diagram with the Eu ordering along the  $c$ -axis; for this direction superconductivity coexists with FM. We sketch such a phase diagram in Fig. 4, where we distinguish between the Eu net magnetization along the  $a$ - and  $c$ -axis. This causes implications that are in particular interesting for theoretical considerations about the interplay of magnetism and superconductivity, as superconductivity in pnictides is often considered as quasi-two-dimensional.

On the basis of in-plane magnetization measurements of  $\text{EuFe}_2(\text{As}_{1-x}\text{P}_x)_2$  single crystals, Jeevan *et al.*<sup>11</sup> proposed a phase diagram that includes FM  $\text{Eu}^{2+}$  ordering for high P content. Assuming that the sample was perfectly oriented with  $H \parallel ab$ , this suggests the spin alignment displayed in Fig. 4 for  $x = 1$ . This is supported by the fact that the hysteresis continues to open with increasing P substitution,<sup>11</sup> while the canting angle already saturates at  $x = 0.2$ .<sup>12</sup>

There is still some discussion about the actual coupling mechanism between the Eu layers. Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction might play an important role (although it is not clear what happens in the superconducting state), but other mediation via the Fe layers is also possible, since direct exchange and dipolar interaction can be ruled out. When going from  $\text{EuFe}_2\text{As}_2$  to  $\text{EuAs}_2\text{P}_2$  the  $a$  and  $c$  axes decrease by 2.3% and 7.3%, respectively.<sup>16</sup> The reduction of the unit-cell volume and the change of the Fermi surface with pressure<sup>14,17</sup> could turn an interlayer RKKY coupling from AFM to FM.<sup>6</sup>

Field-dependent magnetization measurements ranging up to several Tesla can be also explained by the  $\text{Eu}^{2+}$  spin alignment displayed in Fig. 4 and indicate FM interlayer coupling at higher pressure. In  $\text{EuFe}_2\text{As}_2$  the magnetic behaviors for  $H \parallel ab$  and  $H \parallel c$  differ significantly.<sup>3</sup> While in both directions saturation is achieved around 1 T, a step-like magnetization curve appears only in the case of  $H \parallel ab$ . At low field strength, the  $\text{Eu}^{2+}$  spins start to realign, but keep their AFM orientation in adjacent planes; above a kind of spin-flip field the orientation of the spins parallel to the external field wins over the AFM interlayer coupling. In the case of  $H \parallel c$ , however, we propose that such magnetization behavior does not appear since there is no AFM ordering in the  $c$ -direction that has to be broken (Fig. 4). According to our model, the step-like behavior of the magnetization with  $H \parallel ab$  should become weaker as the canting angle of the  $\text{Eu}^{2+}$  spins out of the  $ab$ -plane grows with pressure. For larger canting angles, it gets more and more energetically favorable to orient the spins directly parallel to the external field instead of keeping the AFM ordering. In the case of the FM ordered phase (Fig. 4,  $x = 1$ ), the step-like behavior vanishes. Actually, this magnetization dependence was observed for  $\text{EuFe}_{2-x}\text{Ni}_x\text{As}_2$ , with a weak step in the case of  $x = 0.03$ , which disappears for higher dopings.<sup>6</sup>

Pressure-dependent susceptibility measurements would help to identify the correlations between the  $\text{Eu}^{2+}$  ordering and other phase transitions. It is quite surprising that the tilting angle of the  $\text{Eu}^{2+}$  moments

stays the same, when the SDW is completely suppressed (Fig. 4).<sup>12</sup> This infers that the itinerant AFM phase of the FeAs layers, with the magnetic moments being aligned within the *ab*-plane,<sup>1</sup> does influence the  $\text{Eu}^{2+}$  ordering. It is unlikely that the minor structural phase transition between the orthorhombic and tetragonal phase, taking place at approximately the same P content, has some influence on the canting angle.

Understanding the alignment of the  $\text{Eu}^{2+}$  magnetic moments will also reveal more information on the interplay between magnetism and superconductivity. One interesting feature appearing in the Eu 122 pnictides is a resistivity re-entrance in the superconducting phase near the  $\text{Eu}^{2+}$  magnetic ordering temperature.<sup>7,8,11</sup> In  $\text{Eu}(\text{Fe}_{0.89}\text{Co}_{0.11})_2\text{As}_2$  the  $\text{Eu}^{2+}$  are ordered AFM in the *a*-direction. The superconducting re-entrance can be suppressed with an external magnetic field in the *ab*-plane, while a magnetic field  $H \parallel c$  has no influence on the re-entrance.<sup>7</sup> We do not understand yet, why the AFM  $\text{Eu}^{2+}$  ordering destroys the superconductivity, while it can coexist with the field-induced FM. Nevertheless our model allows us to explain why a magnetic field applied along the *c*-direction has no appreciable influence: it only weakens the spin components in the *ab*-plane without destroying the AFM ordering itself. It should also be noted that for several Eu 122 compounds, susceptibility measurements show additional features below the pronounced AFM or FM Eu ordering, which could have the same origin as the resistivity re-entrance.<sup>6,7,12</sup> Here we want to point out that Ahmed *et al.*<sup>18</sup> observe a significant enhancement of the spin moment on the Fe *3d*

electrons in  $\text{EuFe}_2(\text{As}_{0.73}\text{P}_{0.27})_2$  at  $T = 18$  K. Together with the ordered  $\text{Eu}^{2+}$  moments, the internal magnetic field can then exceed the superconducting upper critical field leading to the re-entrance of resistivity.

#### IV. CONCLUDING REMARKS

Analyzing measurements of the magnetic properties of various Eu 122 compounds we propose that the alignment of the localized  $\text{Eu}^{2+}$  magnetic moments in  $\text{EuFe}_2(\text{As}_{1-x}\text{P}_x)_2$  changes with pressure. In the parent compound  $\text{EuFe}_2\text{As}_2$ , the spins are not simply antiferromagnetically aligned in adjacent *ab*-planes but canted by a few degrees, causing a small ferromagnetic component in *c*-direction. When the interlayer coupling changes with pressure, the canting increases until the SDW in the FeAs subsystem is suppressed and superconductivity sets in. There is a coexistence of superconductivity with antiferromagnetism along the *a*-direction and ferromagnetism along the *c*-axis. At even higher pressure, the interlayer coupling switches to a ferromagnetic one.

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- <sup>1</sup> D. C. Johnston, Adv. Phys. **59**, 803 (2010).
  - <sup>2</sup> H. S. Jeevan, Z. Hossain, D. Kasinathan, H. Rosner, C. Geibel, and P. Gegenwart, Phys. Rev. B **78**, 092406 (2008).
  - <sup>3</sup> S. Jiang, Y. Luo, Z. Ren, Z. Zhu, C. Wang, X. Xu, Q. Tao, G. Cao and Z. Xu, New J. Phys. **11**, 025007 (2009).
  - <sup>4</sup> Y. Xiao, Y. Su, M. Meven, R. Mittal, C.M.N. Kumar, T. Chatterji, S. Price, J. Persson, N. Kumar, S.K. Dhar, A. Thamizhavel, and Th. Brueckel, Phys. Rev. B **80**, 174424 (2009).
  - <sup>5</sup> J. Herrero-Martín, V. Scagnoli, C. Mazzoli, Y. Su, R. Mittal, Y. Xiao, T. Brueckel, N. Kumar, S.K. Dhar, A. Thamizhavel, and L. Paolasini, Phys. Rev. B **80**, 134411 (2009).
  - <sup>6</sup> Z. Ren, X. Lin, Q. Tao, S. Jiang, Z. Zhu, C. Wang, G. Cao and Z. Xu, Phys. Rev. B **79**, 094426 (2009).
  - <sup>7</sup> S. Jiang, H. Xing, G. Xuan, Z. Ren, C. Wang, Z. A. Xu and G. Cao, Phys. Rev. B **80**, 184514 (2009).
  - <sup>8</sup> Z. Ren, Q. Tao, S. Jiang, C. Feng, C. Wang, J. Dai, G. Cao and Z. Xu, Phys. Rev. Lett. **102**, 137002 (2009).
  - <sup>9</sup> C. F. Miclea, M. Nicklas, H. S. Jeevan, D. Kasinathan, Z. Hossain, H. Rosner, P. Gegenwart, C. Geibel, and F. Steglich, Phys. Rev. B **79**, 212509 (2009).
  - <sup>10</sup> T. Terashima, M. Kimata, H. Satsukawa, A. Harada, K. Hazama, S. Uji, H. S. Suzuki, T. Matsumoto, and K. Murata, J. Phys. Soc. Jpn. **78**, 083701 (2009).
  - <sup>11</sup> H. S. Jeevan, D. Kasinathan, H. Rosner and P. Gegenwart, Phys. Rev. B **83**, 054511 (2011).
  - <sup>12</sup> I. Nowik, I. Felner, Z. Ren, G. H. Cao and Z. A. Xu, J. Phys.: Condens. Matter **23**, 065701 (2011).
  - <sup>13</sup> D. Wu, N. Barišić, N. Drichko, S. Kaiser, A. Faridian, M. Dressel, S. Jiang, Z. Ren, L.J. Li, G.H. Cao, Z.A. Xu, H.S. Jeevan, and P. Gegenwart, Phys. Rev. B **79**, 155103 (2009).
  - <sup>14</sup> D. Wu, G. Chanda, H. S. Jeevan, P. Gegenwart, and M. Dressel, Phys. Rev. B **83**, 100503(R) (2011).
  - <sup>15</sup> Y. Xiao, Y. Su, W. Schmidt, K. Schmalzl, C. M. N. Kumar, S. Price, T. Chatterji, R. Mittal, L. J. Chang, S. Nandi, N. Kumar, S. K. Dhar, A. Thamizhavel and T. Brueckel, Phys. Rev. B **81**, 220406(R) (2010).
  - <sup>16</sup> C. Feng, Z. Ren, S. Xu, S. Jiang, Z. A. Xu, G. Cao, I. Nowik, I. Felner, K. Matsubayashi and Y. Uwatoko, Phys. Rev. B **82**, 094426 (2010).
  - <sup>17</sup> S. Thirupathaiah, E. D. L. Rienks, H. S. Jeevan, R. Ovsyannikov, E. Slooten, J. Kaas, E. van Heumen, S. de Jong, H. A. Duerr, K. Siemensmeyer, R. Follath, P. Gegenwart, M. S. Golden, and J. Fink, arXiv:1007.5205.
  - <sup>18</sup> A. Ahmed, M. Itou, S. Xu, Z. Xu, G. Cao, Y. Sakurai, J. Penner-Hahn and A. Deb, Phys. Rev. Lett. **105**, 207003 (2010).